LITERATURE CITED

Abel, E., "The Vapor Phase Above the System Sulfuric Acid-Water," *J. Phys. Chem.*, **50**, 260 (1946).

Bodenstein, M., and M. Katayama, "Die Dissoziation von Hydratischer Schwefelsaure und von Stickstoffdiozyd," *Z. Elektrochem.*, **15**, 244 (1909).

Giauque, W. F., E. W. Hornung, J. E. Kunzler, and T. R. Rubin, "The Thermodynamic Properties of Aqueous Sulfuric Acid Solutions and Hydrates from 15 to 300°K," *J. Am. Chem. Soc.*, **82**, 62 (1960).

Giguere, P. A., and R. Savoie, "Normal Vibrational Frequencies of H_2SO_4 and D_2SO_4," *ibid.*, **85**, 287-9 (1963).

Gmitro, J. I., and T. Vermeulen, "Vapor-Liquid Equilibria for Aqueous Sulfuric Acid," *AIChE J.*, **10**, 740 (1964).

Greenewalt, C. H., "Partial Pressure of Water Out of Aqueous Solutions of Sulfuric Acid," *Ind. Eng. Chem.*, **17**, 522 (1925).

Haase, R., and M. Rehse, "Ermittlung der Taupunkte von Rauchgasen aus dem Verdampfungsgleichgewicht des Systems Wasser-Schwefelsaure," *Mitt. Ver. Grosskesselbesitzer*, **62**, 367 (1959).

Haase, R., and H. W. Borgmann, "Prazisionmessungen zur Ermittlung von Sauertaupunkten," *Korrosion*, **15**, 47 (1961).

Hornung, E. W., and W. F. Giauque, "The Vapor Pressure of Water Over Aqueous Sulfuric Acid at 25°," *J. Am. Chem. Soc.*, **77**, 2744 (1955).

Lisle, E. S., and J. D. Sensenbaugh, "The Determination of Sulfur Trioxide and Acid Dewpoint in Flue Gases," *Combustion*, **36**, 12 (1965).

Luchinskii, G. P., "Physical-Chemical Study of the H_2O-SO_3 System, I. Equilibrium in the vapor and the liquid phase," *Z. Fiz. Khim.*, **30**, 1207 (1956).

Muller, P., "Beitrag zur Frage des Einflusses der Schwefelsaure auf die Rauchgas-Taupunkttemperatur," *Chem. Ing. Tech.*, **31**, 345-51 (1959).

Snowden, P. N., and M. A. Ryan, "Sulfuric Acid Condensation from Flue Gases Containing Sulfur Oxides," *J. Inst. Fuel*, **42**, 188 (1969).

Wagman, D. D., et al., "Selected Values of Chemical Thermodynamic Properties—Tables for the First Thirty-four Elements in the Standard Order of Arrangement," NBS Technical Note 270-3, 49 (1968).

Manuscript received July 18, 1972; revision received August 16, 1972; paper accepted August 18, 1972.

Dispersed Phase Reactor Model for Predicting Conversion and Mixing Effects

M. A. ZEITLIN and L. L. TAVLARIDES

Department of Chemical Engineering
Illinois Institute of Technology, Chicago, Illinois

A model recently developed by Zeitlin (1971) and Zeitlin and Tavlarides (1972a) combines a Monte Carlo technique, the concepts of drop or bubble coalescence and breakup in a turbulent flow field, and a description of the actual flow patterns and particle movements to describe agitated two phase dispersions. The model was applied by Zeitlin and Tavlarides (1972b, 1972c) to predict unsteady gas absorption with and without reaction and interphase transfer in extractors from limited amounts of data. An extension is presented here to study effects of macromixing and micromixing of the dispersed phase on conversion in a liquid-liquid system when the reactant diffuses from the dispersed to the continuous phase and zero, pseudo first- or second-order reaction occurs in the continuous phase. The cases of complete segregation, intermediate drop mixing (at various rev./min.), and pseudo complete drop mixing are compared.

Previous techniques to describe agitated dispersions were largely applied to systems in which the reaction takes place in the dispersed phase. Rietema (1958) calculated the ratio of residence times required to attain a given conversion for the two extremes of no mixing and complete mixing of the dispersed phase of a reactor for a zero-order reaction. Curl (1963) used a simplified population approach method assuming equal size drops with equal coalescence and breakage rates to study zero-order reaction in the dispersed phase of a well stirred flow reactor. Mingheng et al. (1966) employed a similar model in order to study effects of finite interdrop mixing on nonfirst-order reactions. Spielman and Levenspiel (1965) introduced a Monte Carlo technique to study the influence of coalescence on conversion for various reaction orders. Capovani and Tartarelli (1968) used a Monte Carlo technique to study conversion and selectivity for irreversible reactions in series as a function of zero and infinite coalescence rates. This model was modified by Tartarelli et al. (1970) to include two drop sizes and applied to study conversions for irreversible reactions.

Experimental investigations on interphase mass transfer with reaction in the continuous phase for liquid-liquid systems were made by Nagata and Yamaguchi (1960a, 1960b) and Nagata et al. (1960a). Effects of agitation intensity on resistance to mass transfer in the continuous and dispersed phases was studied. A simplified model was presented which could not accurately predict their experimental results at intermediate agitator speeds.

For systems similar to those discussed above, the distribution of concentration among the particle population depends upon circulation rates in the vessel, reaction or mass transfer conditions, rate and number of coalescences

---

Correspondence concerning this paper should be addressed to L. L. Tavlarides. M. A. Zeitlin is with Stauffer Chemical Corporation, Eastern Research Center, Dobbs Ferry, N. Y. 10522.

and redispersions of each drop, and the drop size distribution. Dispersed phase mixing has an important effect on the conversion and selectivity in a given reactor especially for nonuniform particles. The model employed herein attempts to account for these effects in predicting concentration distributions in the dispersed phase, interphase transfer and conversions in liquid-liquid dispersions.

DESCRIPTION OF MODEL AND REACTION SYSTEMS STUDIED

The dispersed phase is assumed to consist of nonuniform spherical drops, only biparticle coalescences occur, and breakup results in formation of two randomly selected nonuniform particles. The breakage and coalescence probabilities are dependent on the region in the vessel.

Macromixing is included in the model via a statistical technique which superimposes both local average hydrodynamics and turbulence intensities upon particle movement. Direction of particle movement may be either random or in the direction of the superimposed particle gross terminal velocity vector with the continuous phase velocity vector. Micromixing is accounted for by droplet breakup and coalescences with complete mixing of droplet contents. Droplet breakup in the impeller region is characterized by a critical value of the Weber number. Values for the model parameters were obtained by Zeitlin and Tavlarides (1972a) by fitting predicted drop size distributions for liquid-liquid dispersions with experimental data. Values of $\beta_{B,CR} = 0.5$, $K_{IR} = 1.0$ and $K_{CR} = 1.0$ employed here correlated experimental results well over a wide range of dispersed phase holdup and system properties.

This study is restricted to batch systems although continuous flow systems can be studied.

Physical properties of a typical liquid-liquid system in which mass transfer and pseudo first-order reaction occurs in the continuous phase were chosen from those available in the literature. The dispersed phase is assumed to consist of 60 weight % iso-valeryl chloride (IVC) and 40 weight % α-nitro propane. The continuous phase is an α-nitro propane saturated water solution. The diffusing reactant IVC is first considered dissolved in the dispersed phase. Contact of the dispersed phase with the water is simulated and IVC is allowed to diffuse from the dispersed phase into the water followed by a hydrolysis reaction.

The rate of hydrolysis of IVC is very fast compared with the rate of diffusion and typifies a pseudo first-order reaction with no diffusing reactant remaining in the continuous phase. The mass transfer rate for this type of a reaction has been shown by Hatta (1932) and Nagata et al. (1959b) to be

$$R = K_B\, A\, c_a^* \qquad (1)$$

where R is the mass transfer-reaction rate, c_a^* is the concentration of reactant at the drop surface, and $K_B = k_1 \beta H'$. Nagata and Yamaguchi (1960b) report a K_B value of 2.67×10^{-4} cm/sec with less than a 5% variation with dispersed phase weight fraction.

In order to study systems with zero and second-order reactions the phases are assumed to have the physical properties as the IVC water system. The continuity equations for the continuous phase are

No drop present

$$\frac{dc_a}{dt} = -\,r_a \qquad (2)$$

Drop present

$$\frac{dc_a}{dt} = k_1 a^* \,(c_a^* - c_a) - r_a \qquad (3)$$

where $r_a = k_r c_a^2$ with $k_r = 3.22 \times 10^2$ liter/g-mole, sec. for second-order reaction; $r_a = k_r = 1.5 \times 10^{-4}$ gm mole/liter, sec. for zero order reaction; and $k_1 = 1.5 \times 10^{-4}$ gm mole/liter, sec. Equation (3) permits one to separate the effects of mass transfer rate, drop concentration, and interfacial surface area on mass transfer rate and conversion.

USE OF SIMULATION

To initiate the simulation particle size distributions, dispersed phase holdup fractions, and interfacial surface areas in various regions of the batch agitated vessel are determined for steady state mixing of the previously described system but assuming no mass transfer or reaction. The average number of simulation program iterations for all drops to coalesce is determined. This information is combined with available correlations for coalescence frequencies in agitated vessels as per Zeitlin (1971), and used to determine the real time per program iteration. The time per iteration is assumed to remain the same irrespective of mass transfer or reaction rates.

Mass transfer and/or reaction is then allowed in each of the individual continuous phase cells. Several important assumptions must be noted here. For the extremely fast pseudo first-order reaction, continuous phase concentration is assumed zero. For reactions of all orders, it is assumed that individual drop interfacial area and concentration remain constant for each individual drop during any particular iteration. This implies the volume and concentration changes as a result of transfer are small for a single time interval. The concentration throughout the drop is also considered uniform. This tends to give transfer rates and conversions that are slightly high, but reduces the computational time in that only one differential equation instead of three coupled differential equations with a moving boundary need be solved for each drop.

The continuous phase cell concentrations are averaged at the end of each program iteration. This assumption of complete backmixing is acceptable according to the experimentation of Nagata and Yamaguchi (1960a, 1960b), Nagata et al. (1960a), and Schindler and Treybal (1968).

The cases of complete segregation (that is, no coalescences or particle breakage) and pseudo-complete mixing (that is, averaging of all drop concentrations after the coalescence and breakage step) are incorporated in the program.

ANALYSIS

The dispersed phase volume concentration distributions can be studied to ascertain the effect of degrees of mixing on conversion and interphase transfer. This concentration distribution function is defined such that

$f_v(y)\,\Delta y$ = fraction of total volume of the dispersed phase with dimensionless concentration in the range $y \pm 1/2\,\Delta y$

and

$$\int_0^1 f_v(y)\,dy = 1 \qquad (4)$$

The effects of nonuniform size distribution are also incorporated by this mode of analysis. Typical sets of distributions for a zero-order reaction were determined for intermediate mixing ($\beta_{B,IR} \alpha r^2$, $\beta_{B,CR} = 0.5$, $K_{IR} = K_{CR} = 1.0$) and are illustrated in Figure 1. At time equals zero particles in all volume ranges have the same dimensionless concentration $y = c_a/c_{a0} = 1$, indicated by a single infinite spike on the drawings. As time increases the distribution peak diminishes and the distribution widens resulting from the differences in the transfer rates between small and large particles. At longer times the distribution again narrows and moves towards an infinite peak at $y = 0$ for complete conversion.

Figures 2 to 4 detail the effects of micromixing on the dispersed phase volume concentration distribution for a second order reaction. The cases of pseudo-complete mixing, intermediate mixing, and complete segregation are compared at different reaction times. Multiple peaks in the concentration volume distribution for segregated systems are readily noticeable. These are caused by large drops present in the initial size distribution amounting to less than 1% of the total number of drops but containing approximately 20% of the dispersed phase volume. Peaks are also found in the distribution for intermediate mixing and are a result of partial segregation effects. They are dissipated due to dispersed phase mixing. These results illustrate how this model can be employed to predict the extent of the reaction not only globally but locally. One can then estimate the degree of agitation and contact time necessary to ensure that all drops have reached a certain level of concentration. The practical applications of this utility are obvious.

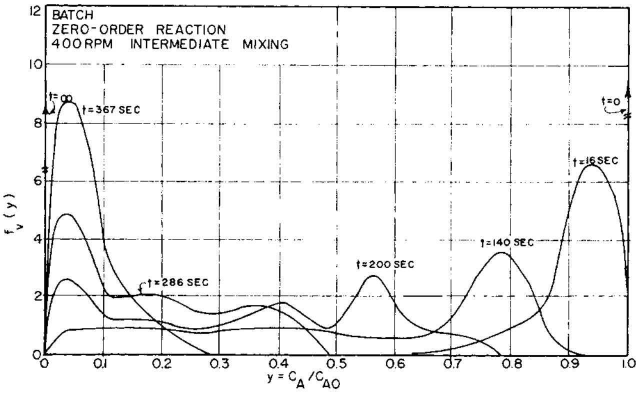

Fig. 1. Volumetric dispersed phase concentration distribution (VDPCD) versus time; $k_r = 1.5 \times 10^{-4} \dfrac{\text{g-mole}}{\text{liter sec}}$; $k_l = 0.05$ cm/sec, $\phi = 0.0063$.

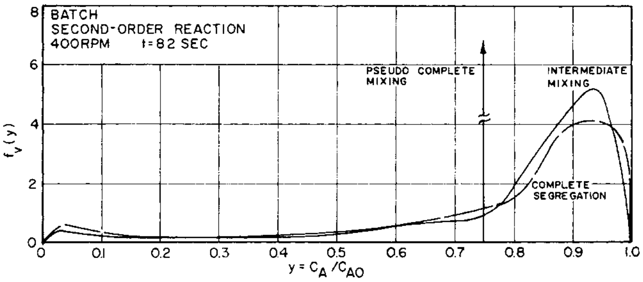

Fig. 2. Volumetric dispersed phase concentration distribution (VDPCD) at 82 sec for second-order reaction in continuous phase; $k_r = 3.22 \times 10^2 \dfrac{\text{liter}}{\text{g-mole sec}}$; $k_l = 0.05$ cm/sec; $\phi = 0.0063$.

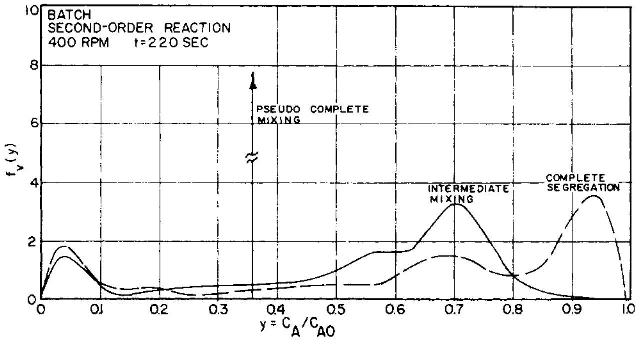

Fig. 3. Volumetric dispersed phase concentration distribution (VDPCD) at 220 sec for second-order reaction in continuous phase; $k_r = 3.22 \times 10^2 \dfrac{\text{liter}}{\text{g-mole sec}}$; $k_l = 0.05$ cm/sec; $\phi = 0.0063$.

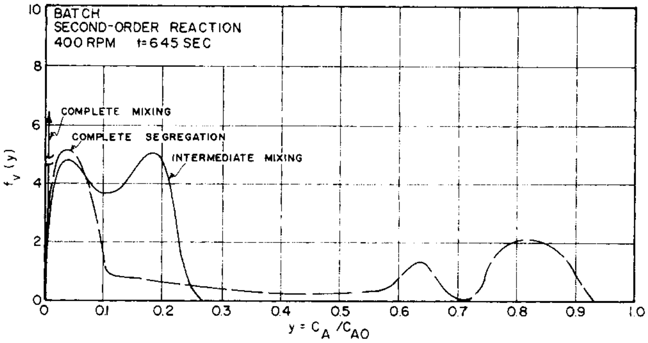

Fig. 4. Volumetric dispersed phase concentration distribution (VDPCD) at 645 sec for second-order reaction in continuous phase; $k_r = 3.22 \times 10^2 \dfrac{\text{liter}}{\text{g-mole sec}}$; $k_l = 0.05$ cm/sec; $\phi = 0.0063$.

One may study the effects of micromixing on reactant transfer by examining the fraction of original reactant still remaining in the dispersed phase. Transient data for this fraction, $1 - X_A$, are illustrated in Figure 5. Although not shown, for all reaction orders the extraction rate is greatest for the pseudo-completely mixed system and lowest for the completely segregated system. This occurs because the transfer rate is proportional to the product of the interfacial area times interfacial concentration summed over all particles. This sum has its smallest value for the completely segregated systems. These are micromixing and particle size distribution effects since batch systems are studied. If the particles were uniform the sum of interfacial area times interfacial concentration over these particles would be equal at any level of mixing for all values of time.

Effects of rev./min., (that is, both macromixing and micromixing) on reactant remaining in the dispersed phase for the pseudo first-order reaction case are also demonstrated in Figure 5. The increased extraction rate at the higher rev./min. value is due to the increase in interfacial area and dispersed phase mixing at this rpm.

Calculations were done on the Univac 1108/4700 digital computer system. Computation time was approximately 6 min. for each of the reported concentration-volume distributions.

DISCUSSION AND CONCLUDING REMARKS

A Monte Carlo model recently developed to simulate dispersed phase turbulently agitated vessels is extended to include mass transfer from the dispersed phase to the continuous with reaction in the continuous phase. Plots of the normalized dispersed phase volume concentration distributions for various reaction times indicate how the degree of mixing affects the concentration distributions of reactant in the dispersed phase. The model can be employed to predict the extent of reaction both globally and locally.

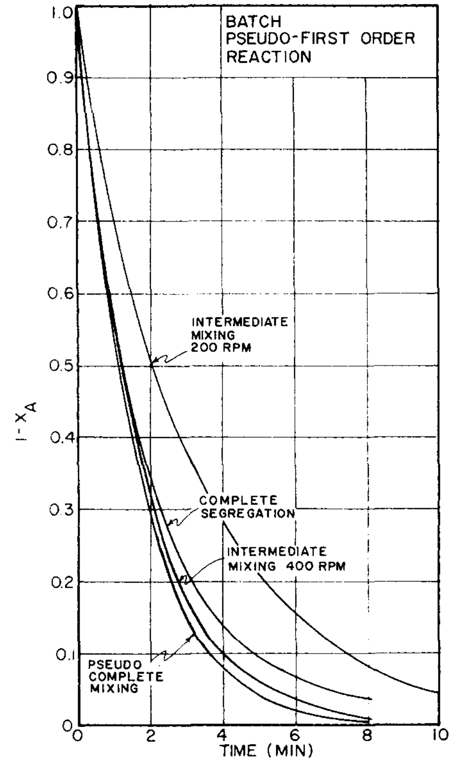

Fig. 5. Reactant remaining versus time and rev./min. for pseudo-first-order reaction in continuous phase; $\phi = 0.0063$.

The contact time and agitation necessary to be sure that all drops have reached a certain concentration range can also be estimated.

The concentration distributions for the cases of complete segregation, intermediate mixing, and pseudo complete mixing indicate the inaccuracies that may result by assuming uniform particle sizes. When dispersed phase mixing occurs, the process of averaging the concentration spread among small and large drops results in an increase of transfer rates. Since all drops have identical residence time distributions (batch reactor), dispersed phase mixing would have no effect on transfer rates in dispersions of uniform size drops.

ACKNOWLEDGMENT

The authors wish to express gratitude to the National Science Foundation for a Predoctorial Traineeship granted to M. A. Zeitlin and to the Department of Chemical Engineering and the School of Engineering of Illinois Institute of Technology for the general support given for conducting the research.

The authors would like to further acknowledge and express gratitude to the National Science Foundation for partial support of the work through NSF Research Initiation Grant GK-27903.

NOTATION

a^* = interfacial area per unit volume, cm^2/cm^3
A = total interfacial area, cm^2
c = molar concentration, mol/l
D = impeller diameter, cm
f_v = function defined in Equation (4)
H' = Henry's law constant
k_l = continuous phase mass transfer coefficient, cm/sec
k_r = reaction rate constant, l/mole sec or mole/l sec
K_B = combined transfer coefficient, cm/sec
K_{CR} = coalescence efficiency in circulation region
K_{IR} = coalescence efficiency in impeller region
N = impeller speed
N_{We} = impeller Weber number, $(D^3N^2\rho^c)/\sigma$
t = time, sec
X = mole fraction of reactant transferred from dispersed phase
y = dimensionless concentration, c_a/c_{a0}

Greek Letters

β = Hatta number
$\beta_{B,\,CR}$ = breakage efficiency in circulation regions
$\beta_{B,\,IR}$ = breakage efficiency in impeller region
ρ = density of fluid, gm/cm^3
σ = interfacial tension, dynes/cm
ϕ = dispersed phase holdup fraction

Superscripts

c = continuous phase
d = dispersed phase
$*$ = in continuous phase at interface

LITERATURE CITED

Capovani, M., and R. Tartarelli, "Reazioni in Serie in Fase Dispersa," *Ing. Chim. Ital.*, **4**, 152 (1968).

Curl, R. L., "Dispersed Phase Mixing: I Theory and Effect in Simple Reactors," *AIChE J.*, **9**, 175 (1963).

Hatta, S., "On the Absorption Velocity of Gases by Liquids, II Theoretical Considerations of Gas Absorption due to Chemical Reaction," *Techn. Rep. Tohoku. Imp. Univ.*, **10**, 613 (1932).

Ming-heng, C., C. Liang-heng, and Y. Wei-Kang, "Mixing of Dispersed Drops in Agitated Continuous Liquid-Liquid Reaction Systems", *Sci. Sinica*, **15**, 123 (1966).

Nagata, S., and I. Yamaguchi, "Effect of Agitation for Mass Transfer in Liquid-Solid Heterogeneous Reaction Systems," *Chem. Eng. Japan*, **24**, 736 (1960a).

———, "Mass Transfer and Chemical Reaction in Liquid-Liquid Agitation Systems," Memoirs of the Faculty of Eng., Kyoto Univ., **22**, 249 (1960b).

Nagata, S., I. Yamaguchi, and M. Harada, "Mass Transfer and Chemical Reaction in Liquid-Liquid Systems-Agitation Effect on the Mixing of the Inner Part of Droplets," *Chem. Eng. Japan*, **24**, 742 (1960a).

———, "Rate of Solution of Solid Particles Followed by Chemical Reaction in Agitated Vessel," Memoirs Faculty of Eng., Kyoto Univ., **21**, 275 (1959b).

Rietema, K., "Heterogeneous reactions in the Liquid Phase: Influence of Residence time Distribution and Interaction in the Dispersed Phase," *Chem. Eng. Sci.*, **8**, 103 (1958).

Schindler, H. D., and R. E. Treybal, "Continuous Phase Mass Transfer Coefficients for Liquid Extraction in Agitated Vessels," *AIChE J.*, **14**, 790 (1968).

Spielman, L. A., and O. Levenspiel, "A Monte Carlo Treatment for Reacting and Coalescing Dispersed Phase Systems," *Chem. Eng. Sci.*, **20**, 247 (1965).

Tartarelli, R., M. Capovani, and S. Tristolini, "Simulazione di un Reattore Agitato Liquido-Liquido con Reazione in Fase Dispersa," *Ing. Chim. Ital.*, **6**, 85 (1970).

Zeitlin, M. A., "Description of Agitated Dispersions with Mass Transfer and/or Reaction," Ph.D. thesis, Ill. Inst. Technology, Chicago (1971).

———, and L. L. Tavlarides, "Fluid-Fluid Interactions and Hydrodynamics in Agitated Dispersions: A Simulation Model," *Can. J. Chem. Eng.*, **50**, 207 (1972a).

———, "On Fluid-Fluid Interactions and Hydrodynamics in Dispersed Phase CSTR's: Prediction of Local Concentrations, Transfer Rates, and Reaction Conversions," in Proc. 5th European (2nd Intern.) Symp. Chem. Reaction Eng., Amsterdam, Holland (1972b).

———, "Prediction of Mass Transfer Coefficients, Local Concentrations and Binary and Ternary Mass Transfer Rates for Extractors," *Ind. Eng. Chem., Process Design Develop.*, **11**, 532 (1972).

Manuscript received July 24, 1972; revision received August 7, 1972; paper accepted August 7, 1972.